Final Project Report for DE-FG02-05ER15752

Electrochemical Synthesis of Polycrystalline Semiconductor Electrodes with Controlled Compositions and Morphologies for Use in Solar Fuel Production

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I. MAJOR RESEARCH ACCOMPLISHMENT DURING JUNE 2011-MAY 2012

The major goal of our research during the previous funding period was to gain the ability in electrochemical synthesis to precisely control compositions and morphologies of various oxide-based polycrystalline photoelectrodes in order to establish the composition-morphology-photoelectrochemical property relationships while discovering highly efficient photoelectrode systems for use in solar energy conversion. The most significant achievements made during June 2011-May 2012 are summarized below.

1. Development of Porous n-type $BiVO_4$ Photoanode for Efficient and Stable Solar Water Oxidation

Bismuth vanadate ($BiVO_4$), an n-type semiconductor, has been recently identified as a promising photoanode for use in a photoelectrochemical water splitting cell. It has a direct bandgap of 2.4 eV and an appropriate valence band position for O_2 evolution. In addition, the conduction band of $BiVO_4$ is located very near the H_2 evolution potential, allowing the photocurrent onset to occur very near 0.0 V vs. RHE. Due to this feature, $BiVO_4$ can generate much higher photocurrent in the low bias region than other photoanodes having a smaller bandgap but a more positive conduction band edge. When a photoanode is coupled with a photocathode in a photoelectrochemical diode assembly, having an early photocurrent onset and a high fill factor for both half reactions (O_2 production and H_2 production) are critical for achieving an overall operating current and, therefore, a high solar-to-hydrogen conversion efficiency.

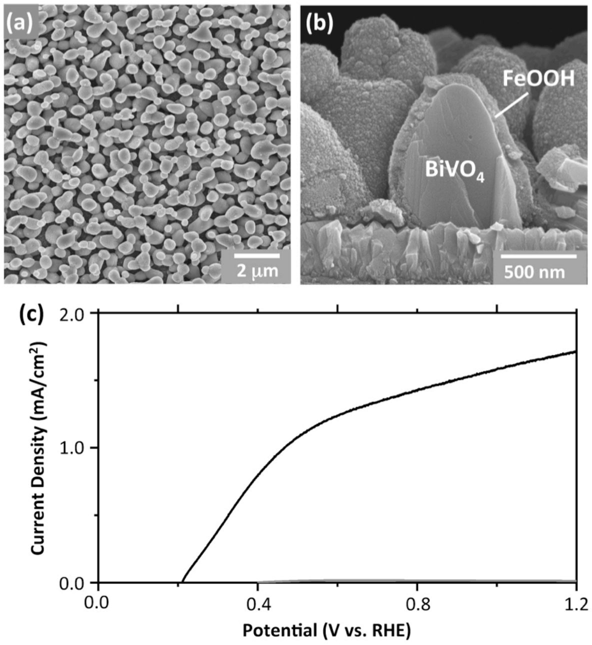

Figure 1. (a) SEM of porous $BiVO_4$ electrode and (b) side-view SEM of $BiVO_4$/FeOOH electrode showing a conformal coating of FeOOH on $BiVO_4$; (c) *J-V* characteristics of $BiVO_4$/FeOOH photoanode in 0.1 M phosophate buffer (pH 7) (AM 1.5 G, 100 mW/cm^2 illumination). Dark current is shown as a gray line.

We have developed a new electrochemical synthesis route that can produce highly porous $BiVO_4$ electrodes that show a record high performance for solar water oxidation (Figure 1). When combined with FeOOH oxygen evolution catalyst (OEC), the porous $BiVO_4$ films showed a remarkable photoelectrochemical performance, achieving the maximum power point at 0.55 V vs. RHE with photocurrent of 1.17 mA/cm^2. This outstanding performance was possible due to the combination of the very negative flatband potential of $BiVO_4$, the porous structure of $BiVO_4$ minimizing electron-hole recombination, and FeOOH being able to improve the water oxidation kinetics almost to the level of sulfite oxidation. The promising and stable solar water oxidation performance achieved by the system prepared by simple synthesis procedures using only non-precious elements presents enormous potential to achieve efficient solar water oxidation by further optimizing morphologies and compositions of the $BiVO_4$-based photoanodes.

2. Development of p-type $CuFeO_2$ Photocathode for Solar Hydrogen Production

Among various semiconductor photoelectrodes, metal oxides hold the most promise in terms of long-term stability and easy processability. However, most of the well-studied oxide electrodes that can utilize visible light for solar water splitting are n-type with the conduction band edge not suitable for hydrogen production. In order to photoelectrolyze water using these materials, application of an external bias or coupling them with a p-type semiconductor electrode having a suitable conduction band position to form photoelectrochemical diodes is necessary. Most p-type semiconductor electrodes extensively studied to date are not oxide-based materials (e.g. Si, GaAs, GaP, $GaInP_2$), which are relatively difficult to process. Therefore, there is a tremendous interest in identifying and preparing cost-effective p-type oxide-based photocathodes with bandgaps that absorb visible light, good charge transport properties, and suitable conduction band positions for hydrogen production.

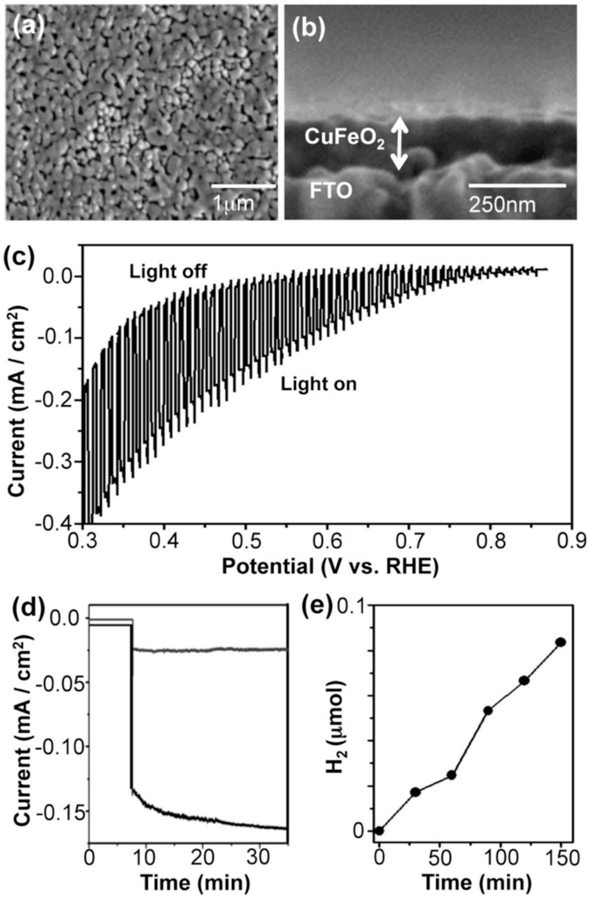

Figure 2. (a) Top-view and (b) side-view SEM image of annealed $CuFeO_2$ film; (c) LSV measured with chopped light (AM 1.5G, 100 mW/cm^2) in 1 M NaOH purged with Ar (scan rate, 10 mV/s), (d) photocurrent measured at 0.6 V vs. RHE in 1 M NaOH purged with Ar (gray) and O_2 (black) (AM 1.5G, 100 mW/cm^2), (e) GC detection of hydrogen generated from $CuFeO_2$ at 0.6 V vs. RHE in 1 M NaOH purged with O_2 under *ca.* 400 mW/cm^2 illumination with an AM 1.5G filter. The addition of O_2 as electron scavenger prevented electron accumulation at the $CuFeO_2$/electrolyte interface and, therefore, photocorrosion of $CuFeO_2$ that is poorly catalytic for H_2 production. This allowed for a longer period of H_2 production and detection of H_2 although the portion of photocurrent associated for H_2 was limited.

We have newly developed a simple electrodeposition route to produce a p-type $CuFeO_2$ electrode which has a bandgap energy of 1.5-1.6 eV and a suitable conduction band position to photoreduce water to H_2. $CuFeO_2$ has a ABO_2-type delafossite structure (A = monovalent ions such as Cu^+ and Ag^+; B= trivalent ions such as Al^{3+}, Ga^{3+}, Fe^{3+}, Mn^{3+}). Delafossite compounds containing Cu^+ ions were reported to have high hole mobilities due to strong covalent nature of the Cu-O bonds. Owing to this feature, delafossites containing Cu^+ ions having a wide bandgap energy (> 3.2 eV) have been studied as optically transparent conductors. However, only a handful of delafossites having a narrow bandgap (< 2 eV) have been investigated for solar energy conversion to date.

Our study demonstrated that $CuFeO_2$

electrodes can photoelectrochemically produce H_2 while absorbing the entire range of the visible spectrum (Figure 2). Modifying the deposition conditions or developing other methods to generate thicker and higher surface area $CuFeO_2$ electrodes as well as identifying and placing proper H_2 evolution catalysts on the $CuFeO_2$ surface will be the future direction to prepare more efficient $CuFeO_2$ photocathodes for a photoelectrochemical water splitting cell. The use of p-$CuFeO_2$ as a photocathode for CO_2 reduction is also under investigation where its poor catalytic property for H_2 evolution may become an advantageous factor.

3. Junction Studies on Electrochemically Fabricated p-n Cu_2O Homojunction Solar Cells for Efficiency Enhancement

Cu_2O is an abundant, low-cost, and environmentally benign direct band gap semiconductor (E_g = 1.9 - 2.2 eV) that is investigated for use in photovoltaic and photoelectrochemical devices. In this study, p-n Cu_2O homojunction solar cells were electrochemically fabricated by consecutively depositing an n-Cu_2O layer on a p-Cu_2O layer. In order to better understand the Fermi levels of the electrochemically grown polycrystalline p- and n-Cu_2O layers and maximize the overall cell performance, the back and front contacts of the Cu_2O homojunction cells were systematically changed and the I-V characteristics of the resulting cells were examined. Since the Hall effect measurements of the electrochemically prepared Cu_2O layers were not possible due to their high resistivities, the experiments carried out in this study provided one of the few feasible ways to indirectly locate their Fermi levels.

The result summarized in Figure 3 shows that the intrinsic doping levels of the electrochemically prepared p-Cu_2O and n-Cu_2O layer are very low and they made almost Ohmic junctions with Cu metal with which previously studied p-Cu_2O layers prepared by thermal oxidation of Cu foils are known to form Schottky junctions. The best cell performance (η of 1.06%, a V_{OC} of 0.621 V, a I_{SC} of 4.07 mA/cm^2, and a fill factor of 42%) was obtained when the p-Cu_2O layer was deposited on a commercially available ITO substrate as the back contact and a sputter deposited ITO layer was used as the front contact on the n-Cu_2O layer, which is the highest efficiency reported to date for a Cu_2O homojunction cell. With continuing studies on optimizing the Fermi levels and the conductivity of both the electrodeposited p- and n-Cu_2O layers and identifying optimum contacts to Cu_2O layers that can form and maintain ideal Ohmic junctions, further improvement of the p-n Cu_2O homojunction solar cells is expected.

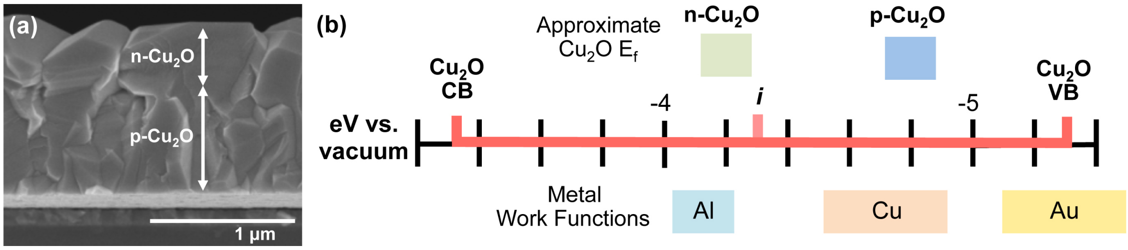

Figure 3. (a) Side view SEM image of p-n Cu_2O homojunction and (b) work functions of contacts (bottom) and approximate Fermi level energies (E_f) of Cu_2O (top). As these Fermi level values are based on the V_{OC}s, the true Fermi level of the n-Cu_2O is expected to be closer to the CB band than what is represented in this figure.

II. LIST OF PUBLICATIONS ATTRIBUTABLE TO THE GRANT DURING JUNE 2011-MAY 2012

The funding resulted in five papers that are listed below. DOE-BES was acknowledged as the only federal funding support for these papers.

1. Spray, R. L. McDonald, K. J.; Choi, K.-S.* "Enhancing Photoresponse of Nanoparticulate a-Fe2O3 Electrodes by Surface Composition Tuning" *J. Phys. Chem C.* **2011**, 115, 3497-3506.
2. McDonald, K. J.; Choi, K.-S.* "Synthesis and Photoelectrochemical Properties of Fe_2O_3/$ZnFe_2O_4$ Composite Photoanodes for Use in Solar Water Oxidation" *Chem. Mater.* **2011**, *23*, 4863-4869.
3. McShane. C. M.; Choi, K.-S.* "Junction Studies on Electrochemically Fabricated p-n Cu_2O Homojunction Solar Cells for Efficiency Enhancement" *Phys. Chem. Chem. Phys.* **2012**, *14*, 6112 – 6118.
4. Read, C. G.; Park, Y.; Choi, K.-S.* "Electrochemical Synthesis of p-type $CuFeO_2$ for Use as a Photocathode in Solar Hydrogen Production" Submitted to *J. Phys. Chem. Lett.* **2012**, 3,1872–1876.
5. McDonald, K. J.; Choi, K.-S.* "Electrochemical Synthesis of BiOI Electrode and Its Conversion to Highly Efficient Porous n-$BiVO_4$ Photoanode for Solar Water Oxidation" Submitted to *Angew. Chem. Int. Ed.* **2012**.